



## Minireview

## Photosynthetic water oxidation: a simplex-scheme of its partial reactions

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Photosynthesis of green plants, algae and cyanobacteria is powered by sunlight. It uses water as ultimate donor of electrons for the reduction of CO<sub>2</sub> to yield carbohydrates. Photosystem II (PS II), a water-plastoquinone oxidoreductase, is the key enzyme of *oxygenic* photosynthesis. It is an integral protein of the thylakoid membrane. PS II is *functionally* bipartite, its photosynthetic reaction centre (RC II) which mediates the primary charge separation is linked to the oxygen evolving complex (OEC) [1,2] which reacts with bound water (see Fig. 1). The net reaction of water oxidation:



operates at an extremely positive midpoint potential of +0.93 eV vs NHE (at the physiological pH of 5 in the lumen of thylakoids) [3]. The oxidising side of RC II, is even more electropositive,  $\geq +1.1$  eV [4]. The large redox span of about 1.25 eV between the primary electron donor in RC II, P<sub>680</sub>, and the primary acceptor (Q<sub>A</sub>), a plastoquinone, is unparalleled by any other reaction centre [5]. In relation to the energy of a quantum of red light, 1.82 eV (wave-

length 680 nm), the efficiency of PS II has been driven to the limits.

Many membrane proteins in photosynthesis and respiration are now fairly well characterised. PS II and, above all, its OEC-portion has remained a tough challenge. The gross structure of the central D1/D2 moiety of PS II is known at a resolution of 8 Å from electron microscopy/diffraction [6]. It bears similarities with the L/M subunits of the reaction centre of purple bacteria and with PS I [7,8]. It is obvious, however, that the intriguing function of the OEC relies on those features which are unique in PS II and have no counterpart in other photosynthetic reaction centres. Further structural analysis of PS II by X-ray crystallography is therefore urgently needed.

The smallest isolated unit which is capable of oxygen evolution contains the D1/D2-heterodimer, at least four further polypeptides, and a total of about 40 chlorophyll molecules [9] (see Fig. 1). D1/D2 hosts the photochemically active chlorophyll molecule(s). P<sub>680</sub>, the primary electron donor, reduces Q<sub>A</sub>, the first of two bound plastoquinone molecules via pheophytin *a*. P<sub>680</sub><sup>+</sup> is, in turn, reduced by the OEC. The latter comprises at least a tetra-atomic manganese cluster (Mn<sub>4</sub>) and a redox active tyrosine residue (D1Tyr161), named Y<sub>Z</sub>. It has been proposed that their midpoint potentials are adjusted by bound Cl<sup>-</sup> and Ca<sup>2+</sup> [10,11], ionic cofactors, which seem to be essential for water oxidation. Y<sub>Z</sub> and some ligands to Mn<sub>4</sub> are located on the D1 subunit [12]. Apparently, the D1-protein carries major portions of both functions of PS II, the photochemical (RC II) and the catalytic one (OEC).

**Abbreviations:** ENDOR, electron nuclear double resonance; EPR, electron paramagnetic resonance; EXAFS, extended X-ray absorption fine structure; FTIR, Fourier transform infrared spectroscopy; Mn<sub>4</sub>, tetra-atomic manganese cluster; OEC, oxygen evolving complex; P<sub>680</sub>, primary donor in PS II; PS II, Photosystem II; Q<sub>A</sub>, bound plastoquinone in PS II; RC II, photosynthetic reaction centre of PS II; XANES, X-ray absorption near edge structure; Y<sub>Z</sub>, tyrosine 161 on subunit D1 of PS II

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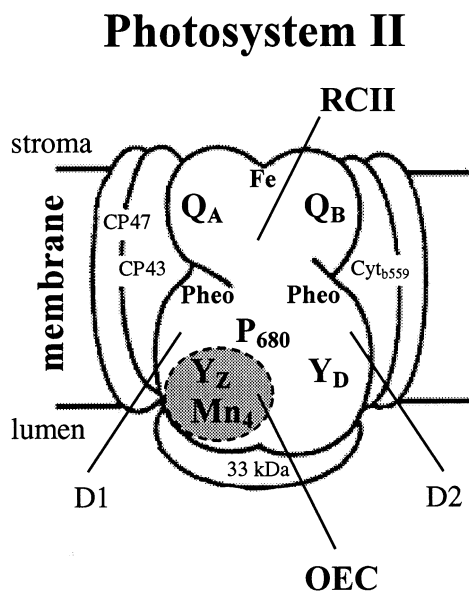


Fig. 1. Schematic drawing of the oxygen evolving core particle of Photosystem II (PS II) which incorporates a photochemical reaction centre (RC II) and the oxygen evolving complex (OEC). This complicated membrane protein is composed of at least seven different polypeptides. The central ones, D1 and D2, contain the redox cofactors of the photochemical activity, the chlorophyll *a*-entity ( $P_{680}$ ), pheophytin *a* (Pheo) and plastoquinones ( $Q_A$  and  $Q_B$ ). D1 contains the redox cofactors of the OEC, namely one tyrosine residue ( $Y_Z$ ) and ligands to the tetra-manganese complex.

It has been a great advantage for studying the OEC that it is self-synchronised in the dark, so that it can be clocked through its partial reactions by short flashes of light. The OEC then steps through five increasingly oxidised states,  $S_0$  to  $S_4$ . Only the last one liberates oxygen and is thereby reset to the state  $S_0$ , ready to undergo another reaction cycle.  $S_1$  is the most stable state after dark adaptation. This model has been derived from the observation of (damped) oscillations of oxygen release with maxima after flashes no. 3, 7, 11, etc. [13]. Time-resolved mass spectrometry has revealed that both  $H_2O$  molecules yielding  $O_2$  are rapidly exchangeable in  $S_2$  and even in the penultimate state,  $S_3$  [14]. This has raised the question whether (bound) water is only processed after the input of the fourth oxidising equivalent into the OEC.

$P_{680}^+$ , which is formed in  $< 1$  ns [15], is reduced by  $Y_Z$  during each reaction step with half-rise times that range between 15 and 300 ns [16].  $Y_Z^{ox}$  is, in turn,

reduced in 30–300  $\mu s$  in the first three steps and in  $\approx 1$  ms in the final oxygen evolving one [17]. The first two oxidising equivalents (that are processed during  $S_0 \Rightarrow S_1$  and  $S_1 \Rightarrow S_2$ ) are stored on manganese itself as inferred from EPR- [18] and from X-ray spectroscopy (XANES) [19]. Both,  $S_0$  and  $S_2$  reveal a multi-line EPR-signal that has been attributed to respective mixed-valence pairs,  $Mn^{II}Mn^{III}$  in the former [20,21] and  $Mn^{III}Mn^{IV}$  in the latter state ([18] and references therein). The chemical nature of the third equivalent (processed during  $S_2 \Rightarrow S_3$ ) is under contention, due to conflicting results from optical and magnetic spectroscopy. Manganese [22,23], or one of its ligands, either histidine [10,24] or bound water [25,26], have been considered as candidates. During the fourth transition,  $S_3 \Rightarrow S_4$ , the oxidising equivalent is transiently stabilised as an oxidised tyrosine [27–29],  $Y_Z^{ox}$ . Its reduction *in milliseconds* coincides with the release of  $O_2$ . The coincidence has been one reason to postulate a role of  $Y_Z^{ox}$  in water oxidation [30,31] which is more active than just being an intermediate electron carrier between  $Mn_4$  and  $P_{680}^+$ .

In artificial water oxidation the first univalent step to produce the hydroxyl radical requires a Gibbs energy of about 2.4 eV (pH 7, in aqueous medium), which is greater than the energy of one quantum of red light (1.8 eV). Renger [32] and Krishtalik [33] have argued that this severe thermodynamic and kinetic constraint might be overcome by coupling the first and the second step to yield a bound peroxide. The transient confinement of the intermediate reaction products in the enzyme pocket raises another complication. It diminishes the entropic stabilisation by dilution of the products. Accordingly, the so called ‘configurational’ potential (grossly speaking, the activation energy) of the overall reaction in the enzyme pocket can be much higher than the averaged +0.93 V (in water at pH 5). Krishtalik [33], who discussed this problem, has argued in favour of at least one hydrogen transfer step as a possible way to compensate the excess energy demand of the reaction. This has prompted the search for potential hydrogen acceptors in the OEC. Some authors, such as Britt and Babcock, have postulated that  $Y_Z^{ox}$  serves in this function [30,31]. Their view has been mainly based on the specific properties of  $Y_Z^{ox}$ , e.g., its hydrogen-bonding interactions and its rotational flexibility, as disclosed by EPR [34,35], ENDOR ([30]

and references therein, [36]) and FTIR [37]. For review see also [38]. One particular argument was related to the then assumed very short distance between manganese and  $Y_Z$ . An appropriate reaction mechanism has been derived [30,31], which is compatible with concepts of inorganic and theoretical chemistry [39,40] but relies on a set of experimentally testable assumptions. That it is still under contention, is owed to the following features. (1) The originally reported very small distance between manganese and  $Y_Z$  of only  $\leq 0.45$  nm [30] has been withdrawn. The same group now favours a distance of at least 0.9 nm [41] in agreement with other authors [42–44], whereas one group favours 1.5–2.0 nm [45]. (2) Most data on distances and on the hydrogen-bonded state of  $Y_Z$  were collected on samples that had been depleted of  $Mn_4$  or  $Ca^{2+}$ . Such treatments deactivate oxygen evolution and affect the inner structure of the OEC [12,46] (see also [47] and references therein). Whether such results bear on the intact OEC is questionable. (3) It has been difficult to integrate into this concept data on proton transfer [48–55], electrogenic charge transfer [16,28,56–58], and proton-steered electron transfer [54,56,59,67,68] (see also review articles [60,61]). There is no evidence for the removal over a long distance of the phenolic proton, when  $Y_Z$  is oxidized by  $P_{680}^+$  in intact PS II. Instead, the proton seems to stay in close vicinity to  $Y_Z^{ox}$  on a neighbouring base, both in oxygen evolving [28,29,59] and, under certain conditions, also in PS II with dysfunctional OEC [27,37,46,62,63,68]. This is not quite what one expects if  $Y_Z$  is charged up to act as a hydrogen acceptor (i.e., an acceptor of  $e^-$  and  $H^+$ ) from water.

The above sketched discrepancies have prompted us to propose another reaction scheme for water oxidation which relies on a minimum set of active elements, is compatible with a wealth of data, and avoids *deus ex machina* elements. The scheme is illustrated in Fig. 2.

We assume that the OEC contains only three redox active cofactors, namely two out of the four manganese atoms plus one tyrosine,  $Y_Z$ . In the most reduced state of the OEC,  $S_0$ , the manganese atom in the distal position relative to  $Y_Z$  is in the  $Mn^{II}$ -state and the proximal one appears as  $Mn^{III}$ . One water molecule is assumed to be loosely bound to  $Mn^{III}$ .  $Y_Z$  is hydrogen-bonded to D1His190

[34,62,63] which results in UV/VIS-spectroscopical properties of  $Y_Z^{\delta-}-H^{\delta+}$ -His190 that are intermediate between the ones of free tyrosine ( $Y_ZH$ ) and tyrosinate ( $Y_Z^-$ ) [47]. The proton shift between  $Y_Z$  and His190 is a prerequisite for the ability of  $Y_Z$  to reduce  $P_{680}^+$  in nanoseconds [32,47,63]. This holds for all transitions from  $S_0$  to  $S_4$ . If this interaction is lost, as in  $Mn_4$ -depleted PS II at acid pH [46,47], in  $Ca^{2+}$ -depleted centres [64,65], or by certain point mutations at D1-His190 [62,63], the electron transfer to  $P_{680}^+$  is slowed by orders of magnitude.

The first electron hole is rapidly moved on from  $Y_Z$  to the distal manganese. It is electrically compensated by the binding of a hydroxyl anion to yield the most symmetrical and stable state of the OEC,  $S_1$ . The abstraction of the second electron from  $Y_Z$  oxidises the distal manganese again, creating  $Mn^{IV}Mn^{III}$ . Our choice of the distal manganese as the target of the first two oxidation steps is tentative. It has been motivated by a distance of at least 0.9 nm between  $Y_Z$  and manganese in  $S_2$  (see above) and by data on local electrochromism [58]. In the state  $S_2$  there are two water molecules bound to the  $Mn_4$ -cluster, both exchangeable, one (here tentatively at the proximal  $Mn^{III}$ ) is exchanged more rapidly (8 ms) than the other one (300 ms) [14].

The series of consecutive reactions and intermediate states ( $S'_3$ ,  $S''_3$ ) after the third abstraction of an electron from the OEC in state  $S_2$  deserve closer inspection. This reaction sequence is distinguished by three properties. (i) The electron transfer to  $Y_Z$  is slower than in the previous transitions and probably kinetically limited by a proton transfer (as apparent from a greater H/D-kinetic isotope effect,  $\approx 2.5$  instead of 1.1 and a larger activation energy ([29] and references therein)). (ii) As soon as the electron hole has reached the OEC it is electrically compensated by proton release into the bulk (as evident from the absence of a long-lived electrochromic transient [10,16,28], and from a larger electrogenicity [57]). (iii) The final site of the oxidizing equivalent is a manganese ligand rather than manganese itself, debatable when considering XANES data alone [19,22], but it is clearly favoured by data on  $K_\beta$ -fluorescence (J. Messinger, personal communication)). Moreover, the fully expressed  $S_3$ -state may have some peroxide character [3,29].

At this point we refrained from invoking in this

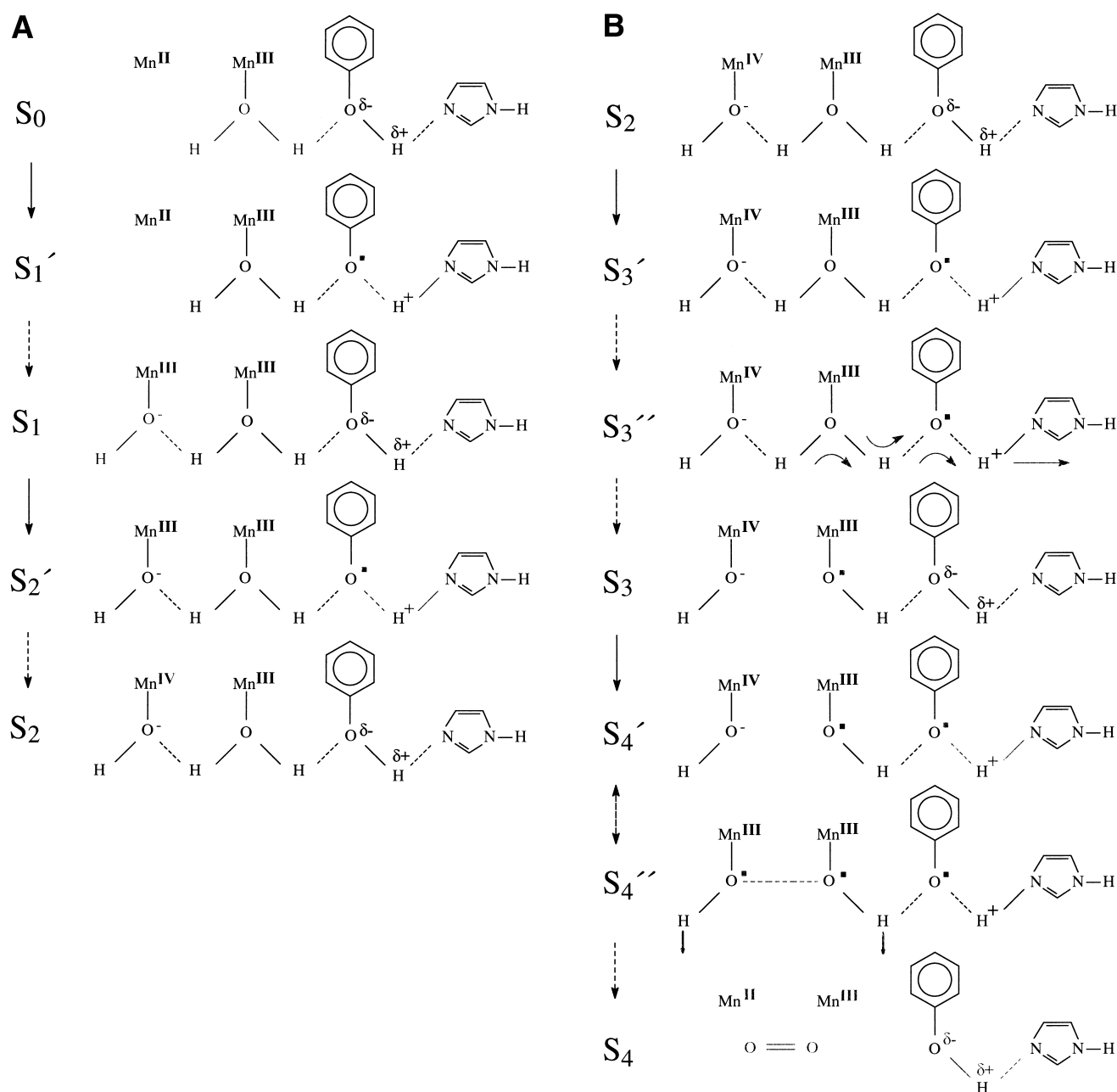


Fig. 2. Tentative model for the reaction sequence of photosynthetic water oxidation. The photochemically driven four-stepped progress involves five increasingly oxidised formal states ( $S_0$ ... $S_4$ ). It is followed by oxygen evolution during the transition from  $S_4$  back to  $S_0$ .  $Y_Z$  is shown as hydrogen-bonded to the proximal bound water, which implies a small distance between  $Y_Z$  and the proximal Mn. The reaction scheme is, however, independent of this assignment, as alternative pathways for the release of water protons are conceivable, different from the here suggested path through  $Y_Z$ .

transition another amino acid cofactor, X, as suggested in previous work (mainly on inhibited PS II) from several laboratories including our own one [10,24,66]. As the spectroscopic features are not very specific in this respect, X may simply be bound

water. It is oxidised into a bound hydroxyl radical and then forms a pre-peroxide state together with the bound hydroxyl anion. The radical/manganese interaction quenches the multiline EPR-signal of the still existing mixed-valence manganese cluster. Still, both

bound water molecules are exchangeable (30 and 500 ms) [14].

The final production of oxygen is initiated by the forth abstraction of an electron from the OEC, producing  $Y_Z^*$ . It is apparent that the only other oxidisable component of the OEC is not the bound hydroxyl anion, but the  $Mn^{III}Mn^{III}$ -peroxide entity, a small fraction of which may be present already in state  $S_3$  (see [29] and references therein). In state  $S_4'$  peroxide is formed but firmly bound and/or so short-lived that it has remained undetected. We suppose that the low probability of the peroxide state (the equilibrium between states  $S_4'$  and  $S_4''$  is poised towards  $S_4'$ ), rather than the velocity of the electron transfer, limits the rate of oxygen evolution.

When considering the tentative reaction sequence in Fig. 2, some paradigms that have caused vivid controversy in the literature may appear questionable if not obsolete. Neither are amino acids, other than tyrosine  $Y_Z$ , needed as redox cofactors nor does  $Y_Z^{ox}$  necessarily release its phenolic proton into the bulk during each transition. What about the dichotomy between the two proposed roles of  $Y_Z^{ox}$ , namely the hydrogen acceptor [30,31,38] versus the electrostatic promoter [29,46]? In our model  $Y_Z$  possibly serves in both functions, as a hydrogen acceptor, but only during the transition  $S_3' \rightarrow S_3''$ , where the bound hydroxyl radical is formed, and as an electrostatic promoter which provides the final overpotential to push the reactions from  $S_3$  to  $S_4$ , the final step which produces oxygen.

Despite of its reduction to a minimum set of elements the proposed reaction scheme appears compatible with most of the available data. With the semi-stationary states  $S_i$  now reasonably well understood, the obvious task for the future is twofold: to resolve (1) the atomic structure, and (2) the chemical nature of the intermediate states,  $S_i'$ .

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